I. THE SYNTHESIS OF 1-BENZYL-1-METHYL-2-MESITOYL-1,2,3,4-TETRAHYDRONAPHTHALENE

II. STERIC HINDRANCE AND THE REACTIVITY OF ENOLATE GRIGNARD REAGENTS

BY

RICHARD JASON HELLMANN

B.S., University of Wisconsin, 1948
M.S., University of Illinois, 1949

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. THE SYNTHESIS OF 1-BENZYL-1-METHYL-2-MESITOYL-1,2,3,4-TETRAHYDRONAPHTHALENE

Introduction

A novel reaction recently investigated by Fuson, Gaertner (1) and Shealy (2) was the addition of benzylmagnesium chloride to 1-methyl-2-mesitoylnaphthalene and subsequent ketonization of the enol formed. It was postulated that the product of the reaction was 1-benzyl-1-methyl-2-mesitoyl-1,4-dihydronaphthalene. If this postulate is correct, the reaction is unprecedented. The present investigation was undertaken in an attempt to elucidate the structure of this compound by an independent synthesis of its hydrogenation product, presumably 1-benzyl-1-methyl-2-mesitoyl-1,2,3,4-tetrahydronaphthalene.

Discussion Of Results

The synthesis of 1-benzyl-1-methyl-2-mesitoyl-1,2,3,4-tetrahydronaphthalene was accomplished in the following manner. Alkylation of ethyl acetoacetate to form ethyl phenethylacetoacetate was effected by use of phenethyl bromide and sodium ethoxide. Cyclization of ethyl phenethylacetoacetate with concentrated sulfuric acid at -20° followed by hydrolysis produced 1-methyl-3,4-dihydro-2-naphthoic acid. Treatment of this acid with phosphorus trichloride gave 1-methyl-3,4-dihydro-2-naphthoyl chloride. Friedel-Crafts acylation of mesitylene with this acid chloride yielded 1-methyl-2-mesitoyl-3,4-dihydronaphthalene. Condensation of this compound with benzylmagnesium chloride and subsequent ketonization produced 1-benzyl-1-methyl-2-mesitoyl-1,2,3,4-tetrahydronaphthalene.

The 1-benzyl-1-methyl-2-mesitoyl-1,2,3,4-tetrahydronaphthalene prepared by the above method proved to be identical with the compound obtained by catalytic hydrogenation of the

product of Fuson, Gaertner and Shealy.

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II. STERIC HINDRANCE AND THE REACTIVITY OF ENOLATE GRIGNARD REAGENTS

Introduction

It is well-known that halomagnesium derivatives of mesityl ketones behave as though they were true Grignard reagents (1,2,3). However, little is known concerning the limitations placed on the reactivity of enolate Grignard reagents by substituents on the *alpha* carbon atoms of these compounds.

It was observed that the enolate Grignard reagent of 1-benzyl-1-methyl-2-mesitoyl-1,2,3,4-tetrahydronaphthalene was resistant to attack, presumably because of steric hindrance. This investigation was undertaken in an attempt to determine which elements of the structure of 1-benzyl-1-methyl-2-mesitoyl-1,2,3,4-tetrahydronaphthalene were primarily responsible for the inactivity of its enolate Grignard reagent.

Discussion Of Results

Steric hindrance in this compound was investigated by synthesizing β-benzyl-β-phenylbutyromesitylene and γ-phenylbutyromesitylene and testing the reactivity of their respective enolate Grignard reagents. The former compound possesses all the structural elements of 1-benzyl-1-methyl-2-mesitoyl-1,2,3,4-tetrahydronaphthalene with the exception of the substituent on the *alpha* carbon atom. The latter compound has

the structure of β-benzyl-β-phenylbutyromesitylene with exception of the methyl and phenyl substituents on the *beta* carbon atom. The enolate Grignard reagents of both these compounds were resistant to attack. Consequently, it is the benzyl group on the *beta* carbon atom of 1-benzyl-1-methyl-2-mesitoyl-1,2,3,4-tetrahydronaphthalene which is primarily responsible for the inactivity of its enolate Grignard reagent.

γ-Ethoxybutyromesitylene and β-methoxypropiomesitylene were synthesized. The enolate Grignard reagent of the ethoxy ketone was found to be inactive while that of the methoxy ketone condensed with acetophenone.

An explanation of these findings, on a basis similar to that utilized by Newman (4) in his *Rule of Six,* has been proposed. This explanation suggests that the reactivity of the *alpha* carbon atom of an enolate Grignard reagent is inhibited if the compound has hydrogen atoms or other substituents in a six-position when the *alpha* carbon is considered the one-position.

Of the mesityl ketones reported in this work and those found in the literature, the compounds which have hydrogen atoms or other substituent groups in the six-position form enolate Grignard reagents that are inactive to attack at the *alpha* carbon atom. Those which do not have such groupings in the six-position are reactive.

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VITA

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